

Hardness of T-carbon: Density functional theory calculations

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(Dated: August 15, 2011)

We revisit and interpret the mechanical properties of the recently proposed allotrope of carbon, T-carbon [Sheng *et al.*, Phys. Rev. Lett., **106**, 155703 (2011)], using density functional theory in combination with different empirical hardness models. In contrast with the early estimation based on the Gao's model, which attributes to T-carbon an high Vickers hardness of 61 GPa comparable to that of superhard cubic boron nitride (*c*-BN), we find that T-carbon is not a superhard material, since its Vickers hardness does not exceed 10 GPa. Besides providing clear evidence for the absence of superhardness in T-carbon, we discuss the physical reasons behind the failure of Gao's and Šimůnek and Vackář's (SV) models in predicting the hardness of T-carbon, residing on their improper treatment of the highly anisotropic distribution of quasi-*sp*³-like C-C hybrids. A possible remedy to the Gao and SV models based on the concept of superatom is suggest, which indeed yields a Vickers hardness of about 8 GPa.

PACS numbers: 64.60.My, 64.70.K-, 62.25.-g, 62.20.Qp

Recently, on the basis of first-principles calculations Sheng *et al.* proposed a carbon allotrope which they named T-carbon¹. Strictly speaking, its actual stability needs a highly large negative pressure which is far beyond currently available technologies. Structurally, this phase can be obtained by substituting each carbon atom in diamond with a carbon tetrahedron (Fig. 1), and thus crystallizes in the same cubic structure of diamond (space group $Fd\bar{3}m$) with the carbon atoms at the Wyckoff site $32e$ (0.0706, 0.0706, 0.0706). It has been noted that T-carbon has a large lattice constant of 7.52 Å and a low bulk modulus of $B = 169$ GPa, only 36.4% of the bulk modulus of diamond¹. In particular, its equilibrium density, 1.50 g/cm³, is the smallest among diamond (cubic and hexagonal diamond)¹, graphite¹, *M*-carbon², *bct*-C₄³, *W*-carbon⁴, *chiral*-carbon⁵ as well as the newly proposed dense *hp3*-, *tI12*- and *tP12*-carbon⁶ phases. This results in an highly porous structural pattern, which can be viewed as a diamond-like array of superatoms (tetrahedral C₄ clusters), as depicted in Fig. 1. Given this peculiar clusterized arrangement of atoms exhibiting a quite low shear modulus of $G = 70$ GPa¹, it is very surprising that T-carbon was predicted to be superhard, with an exceptionally high Vickers hardness (H_v) of 61.1 GPa¹, comparable to that of superhard cubic boron nitride (*c*-BN).

The aim of our present study is to elucidate the origin of this anomalous hardness. We do this by exploring in details the mechanical properties of T-carbon through the application of several different empirical approaches: the Gao's formula⁷, the SV model⁸ and our recently proposed empirical treatment based on the Pugh's modulus ratio⁹. Our systematic analysis provides an unambiguous and physically sound results: T-carbon is not hard. We will show that the conventional application of Gao and SV models leads to a much too high Vickers

hardness, $H_v^{\text{Gao}} = 61.1$ GPa and $H_v^{\text{SV}} = 40.5$ GPa, substantially overestimated with respect to the value obtained using our formalism, $H_v^{\text{Chen}} = 5.6$ GPa. The prediction of a low Vickers hardness in T-carbon is consistent with the estimation of a low shear strength (7.3 GPa along the (100)<001> slip system), which represents the upper bound of the mechanical strength.

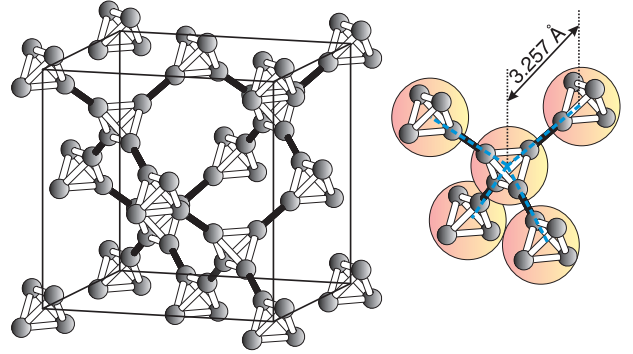


FIG. 1: Lattice structure of T-carbon (space group $Fd\bar{3}m$). By considering each carbon tetrahedron (C₄ unit) as an artificial superatom, the corresponding structure is isotypic to that of diamond. The local environment of each superatom is illustrated in the right panel.

The improper assignments derived by a conventional application of the Gao and SV models can be attributed to the fact that these two models assume that the chemical bonds, which are significant for hardness, are distributed *uniformly* in the lattice. But in T-carbon, as already pointed out by Sheng *et al.*¹, though the carbon atoms are tetrahedrally coordinated and apparently resembling a three-dimensional quasi-*sp*³-like hybrid¹, their bonds are ordered in an extremely anisotropic and

porous framework, highly different from the bonding distribution in ideal sp^3 -hybrid. We propose a remedy to cure the limitations of Gao and SV models in dealing with anisotropic and porous systems by assuming each carbon tetrahedron cluster as an artificial superatom. Indeed, this cluster-like approach leads to low Vickers hardness in the range of 7-8 GPa, in agreement with the estimated value of 5.6 GPa using our proposed model⁹.

All calculations were performed using the Vienna *ab initio* Simulation Package (VASP)¹⁰ in the framework of density functional theory (DFT), and we adopted the Perdew, Burke and Ernzerhof approximation¹¹ to treat the exchange-correlation kernel. Well converged results were obtained using an energy cut-off of 500 eV and a k-point grid $11 \times 11 \times 11$ ¹². The DFT results were then employed as input for the three different hardness empirical models, with which we have computed the Vickers hardness H_v :

(a) Gao's model⁷:

$$H_v^{\text{Gao}} = 350[(N_e^{2/3})e^{-1.191f_i}/(d^{2.5})] \quad (1)$$

where N_e is the electron density of valence electrons per \AA^3 , d is the bond length and f_i is the ionicity of the chemical bond in a crystal scaled by Phillips. As already mentioned, this model gives $H_v^{\text{Gao}} = 61.1$ GPa (Ref. 1).

(b) SV model⁸:

$$H_v^{\text{SV}} = \frac{C}{\Omega} \sqrt{e_i e_i} / (d_{ii} n_{ii}) \quad (2)$$

where C is the constant of 1550 and Ω is the equilibrium volume of T-carbon. $e_i = Z_i/R_i$ represents the reference energy, with Z_i indicating the valence number of element i . For carbon $e_i = 4.121$ (taken from Ref. 8). n_{ii} and d_{ii} are the number of bonds and bonding lengths between atom i . In T-carbon, each carbon has four nearest-neighbors with two different bonding lengths: three intratetrahedron carbon-carbon bonding length of 1.502 \AA and one intertetrahedron bonding length of 1.417 \AA . By using the average bonding length of 1.48075 \AA we obtained $H_v = (1550/26.5785) \times 4.121 / (1.48075 \times 4) = 40.5$ GPa, which is 33.5% smaller than the corresponding Gao's value.¹

(c) Chen's model⁹. This is the empirical formula which we have recently proposed, based on the Pugh's modulus ratio $k=G/B$ ¹³:

$$H_v^{\text{Chen}} = 2(k^2 G)^{0.585} - 3. \quad (3)$$

This model not only reproduced well the experimental values of Vickers hardness of a series of hard materials including all experimentally verified superhard materials (see Fig. 2 and Table I), but also provides a theoretical foundation of Teter's empirical correlation¹⁴ in its simplified form⁹.

Before discussing the results for T-carbon we start by presenting some general considerations regarding the calculation of the Vickers hardness and the trustability of

our proposed model⁹. Hardness is a highly complex property, which depends on the loading force and on the quality of samples (i.e., presence of defects such as vacancies and dislocations). Because Vickers hardness is experimentally measured as a function of the applied loading forces, the saturated hardness value (or experimental load-invariant indentation hardness) is usually considered to be the hardness value of a given material. Therefore, the theoretically estimated Vickers hardness within Gao's, SV's and Chen's models should be directly compared to the experimentally saturated hardness value of polycrystalline materials. An overview on the experimental and theoretical values of H_v for the experimentally verified superhard materials (diamond, *c*-BC₂N, *c*-BN, *c*-BC₅, γ -B₂₈) is summarized in Fig. 2 and Tab. I. The experimental results are highly scattered, reflecting the inherent difficulties in achieving a trustable and precise estimation of hardness. For instance, the reported values for the hardness of diamond, the archetype superhard materials, range from 60 GPa to 120 GPa¹⁶⁻¹⁹. Similar trends have been observed for the other two well-known superhard materials *c*-BC₂N and *c*-BN. The most typical case is probably ReB₂, whose actual hardness has been extensively debated²⁹⁻⁴² after the first value of its Vickers hardness (48 ± 5 GPa at the loading force of 0.49 N) was reported³¹. Depending on different samples, synthetic methods and measurement technique, the obtained values range from 18 to 48 GPa (Table I). In contrast to experiment, theoretical estimations of the Vickers hardness given by different models⁷⁻⁹ agree within few GPa, including the data obtained by our proposed model (Eq. 3). Overall, the comparative trend displayed in Fig. 2 provides robust evidence for the reliability of our proposed formalism⁹.

Now, let's turn the attention to T-carbon. By using the values of the shear and bulk moduli from Ref.1 as input ($B = 169$ GPa and $G = 70$ GPa) for Eq. 3 we obtain a Vickers hardness of 5.6 GPa, dramatically smaller than the corresponding Gao (61.1 GPa) and SV (40.5 GPa) estimations. Furthermore, we noted that Sneddon defined the concept of ideal elastic hardness by $H_{id} = \frac{E \cot \phi}{2(1-\nu^2)}$ where E is Young's modulus, ν is Poisson's ratio and $\cot \phi \approx 0.5$ for the standard pyramid indentation⁴³ and suggested that the real hardness would be $(0.01 \sim 0.2)H_{id}$ at high loads⁴³. Utilizing this definition and the derived $E = 185$ GPa, the real hardness for T-carbon should be in the range from 0.5 GPa to 10 GPa, in agreement with our obtained value. In particular, it still needs to note that the occurrence of this serious discrepancy among the three different methods (Gao's, SV's and Chen's models), which is not observed for the other test cases of Fig. 2 and Table I, urges for a clarification aiming to discern which method provides the more reliable description of the hardness of T-carbon and, consequently, to help us to answer a naturally arising question: is T-carbon a real superhard material?

An useful concept for understanding strong mechanical strength – but still relying on elastic properties – is

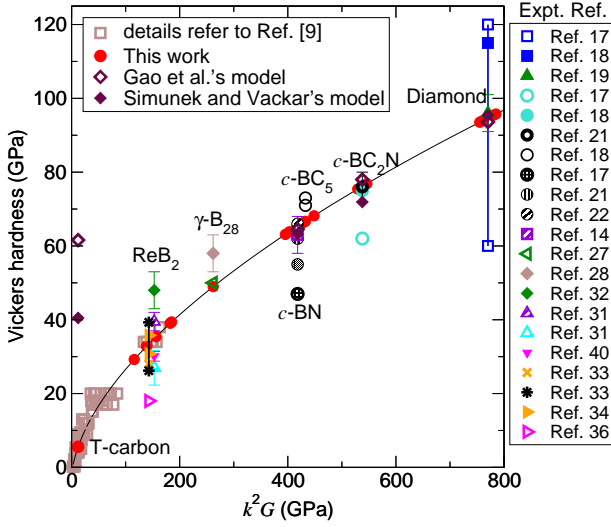


FIG. 2: Vickers hardness H_v as a function of a product ($k^2 G$) of the squared Pugh's modulus ratio ($k = G/B$) and shear modulus (G). The curve corresponds to the empirical relation of Eq. 3 (For other data and more details, see Ref. 9). Elastic moduli and experimental Vickers hardness are collected in Table I. Note the huge discrepancies among the three theoretical estimations for T-carbon.

based on ideal shear and tensile strengths⁴⁵, at which a material is getting unstable under direction-dependent deformation strains⁴⁴. To shed some light on the nature of T-carbon we have thus investigated ideal tensile strength along the $\langle 001 \rangle$ direction and shear strength along the $(100)\langle 001 \rangle$ slip system. We found that a tensile strength of 40.1 GPa along the $\langle 001 \rangle$ direction and a shear strength of 7.3 GPa in the $(100)\langle 001 \rangle$ slip system (see Fig. 3). Therefore, we can conclude that the failure mode in T-carbon is dominated by the shear deformation type in the $(100)\langle 001 \rangle$ slip system. The calculated shear stress of 7.3 GPa basically sets the upper bound on its mechanical strength at zero pressure^{44,45}, because the ideal strength is the stress where a defect-free crystal becomes unstable and undergoes spontaneous plastic deformation. It is well-known that the measurement of hardness has to first encounter the elastic deformation and then experience permanent plastic deformation. Therefore, it can be conjectured that the hardness of T-carbon should not exceed 7.3 GPa. These arguments provide a strong support for our estimated Vickers hardness of 5.6 GPa on the basis of Eq. 3.

In order to gain further insights on this intricate subject and to reach a consistent and satisfactory conclusion on the hardness of T-carbon we consider now the relation between hardness and brittleness on the basis of the Pugh's modulus ratio¹³. There is no doubt that all experimentally verified superhard materials, such as diamond, c -BN, c -BC₂N, γ -B₂₈ and c -BC₅ are intrinsically brittle. As shown in Table I the Pugh's modulus ratio¹³ of these superhard materials ($k = 1.211$ - 1.178 (diamond), 0.999 -

TABLE I: Comparison between measured (H_v^{Exp}) and theoretically computed values of the Vickers' values (in GPa), along with available bulk modulus (B , GPa), shear modulus (G , GPa) and Pugh's modulus ratio $k = G/B$.

	G	B	k	H_v^{Chen}	H_v^{Exp}	H_v^{Gao}	H_v^{SV}
Diamond	536 ^a	442 ^a	1.211	95.7	60-120 ^d	93.6	95.4
	548 ^a	466 ^a	1.178	93.9	115 ^e		
	520 ^b	432 ^b	1.205	93.5	95 \pm 5 ^f		
	535 ^c	443 ^c	1.208	95.4			
c -BC ₂ N	446 ^g	403 ^g	1.107	76.9	62 ^d , 75 ^e	78	71.9
	445 ^c	408 ^c	1.091	75.4	76 \pm 4 ^{e, h}		
c -BC ₅	394 ^t	376 ^z	1.048	66.7	71 ^e , 73 ^e		
	405 ^j	400 ^j	1.014	65.2	47 ^d	64.5	63.2
	403 ^a	404 ^a	0.999	63.8	55 ^h		
	382 ^a	376 ^a	1.017	63.1	62 ^h		
	404 ^k	384 ^k	1.053	68.2	66 ^l		
	409 ^c	400 ^c	1.023	66.2	63 \pm 5 ^c		
γ -B ₂₈	236 ^m	224 ^m	1.054	49.0	50 ⁿ , 58 \pm 5 ^o		
ReB ₂	273 ^p	382 ^p	0.715	32.9	48 \pm 5 ^s		
	273 ^r	383 ^r	0.712	32.8	39.5 \pm 2.5 ^r		
	183 ^r	230 ^r	0.795	29.3	27 \pm 4.7 ^r		
	289 ^x	365 ^x	0.794	39.0	37.2-40.5 ^t		
	283 ^y	264 ^z	0.808	39.4	28 ^t		
	350 ^y	343 ^z	0.769	35.4	39.3-26.2 ^u		
					30.8-35.8 ^v		
					18 ^w		
T-carbon					30.1 \pm 1.3 ^A		
					37 \pm 1.2 ^B		
T-carbon	70 ^C	169 ^C	0.414	5.6		61.1	40.5

^a Ref.¹⁵, ^b Ref.¹⁶, ^c Ref.¹⁴, ^d Ref.¹⁷, ^e Ref.¹⁸, ^f Ref.¹⁹, ^g Ref.²⁰, ^h Ref.²¹, ⁱ Ref.²², ^j Ref.²³, ^k Ref.²⁴, ^l Ref.²⁵, ^m Ref.²⁶, ⁿ Ref.²⁷, ^o Ref.²⁸, ^p Ref.²⁹, ^q Ref.³⁰, ^r Ref.³¹, ^s Ref.³², ^t Ref.³³, ^u Ref.³⁴, ^v Ref.³⁵, ^w Ref.³⁶, ^x Ref.³⁷, ^y Ref.³⁸, ^z Ref.³⁹, ^A Ref.⁴⁰, ^B Ref.⁴¹, ^C Ref.¹.

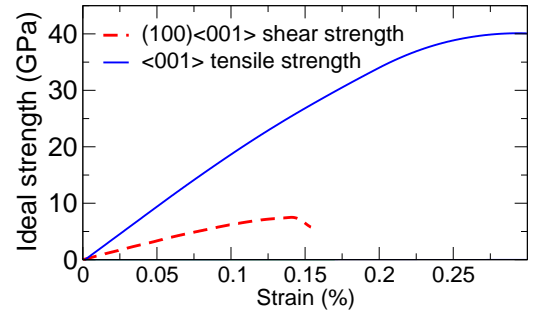


FIG. 3: DFT calculated ideal tensile and shear strengths of T-carbon.

1.053 (c -BN), 1.107 - 1.091 (c -BC₂N), 1.054 (γ -B₂₈) and 1.048 (c -BC₅)) are larger than 1.0. They clearly obey to the empirical relation that considers the Pugh's modulus ratio as an indicator of the brittleness or ductility of materials. The higher k the more brittle (and less ductile) the material is. Pugh still proposed, when k is larger than 0.571 the materials are brittle and with k being less than 0.571 the materials are ductile¹³. This relation has

been extensively applied not only to metals and alloys but also to high-strength materials. In the case of T-carbon, the calculated Pugh's modulus ratio $k = 0.414$ is smaller than 0.571, clearly in the range of ductility. The ductile behavior of T-carbon is a further indication of its non-superhardness.

On the basis of the above consideration we can now understand why T-carbon is not an superhard material. One common feature of superhard materials is that they not only need a three-dimensional network composed of short, strong, and covalent bonds⁴⁶ but also have a *uniform* distribution of strong covalent bonds. The prototypical example is diamond, which is characterized by an isotropic array of tetrahedrally bonded sp^3 carbon atoms. Conversely, in soft graphite the sp^2 -type covalent bonds, though strong, are localized in two-dimensional sheets. At first glance, T-carbon seems to be a good candidate for superhardness since each carbon atom has four nearest-neighboring carbon tetrahedrally bonded by short and strong carbon-carbon covalent bonds. However, due to the extreme-anisotropic arrangement of these carbon-carbon bonds and the associated formation of a large proportion of porosity in lattice space as well as the low density of bonds, the framework of T-carbon be more easily bendable in comparison with that of diamond, as manifested by its low shear strength.

Having this in mind, we can look back Gao's and SV models. Although these two models perform very well for many hard materials, they deliver questionable numbers for T-carbon in sharp contrast with our findings, as we have documented above. The reason for this apparent failure is that in these two models all bonds are treated as *uniformly* distributed in the lattice space. Clearly, this constrain will not affect the predictions for isotropic material but it will be inadequate to describe the hardness of extremely-anisotropic compounds such as T-carbon. However, if we give a closer look to each individual C4 tetrahedron unit (see Fig. 1), the distribution of six strong carbon-carbon covalent bonds within each C4 unit is highly dense. It is therefore trustfully expected, that the Vickers hardness of each individual C4 unit can be comparable (or even harder) to that of diamond because its bonds density and strengths within each C4 unit are higher than those of diamond. The strength and rigidity of each individual C4 unit appear to be such strong that it cannot be broken easily. Based on this fact, in order to render Gao's and SV's meth-

ods applicable to T-carbon, each carbon tetrahedron (C4 unit) is considered to be an artificial superatom (See right panel of Fig. 1). The cubic unit cell of T-carbon consists of eight superatoms and each superatom has four nearest neighbors with the bonding length of $d = 3.257$ Å. In terms of Gao's and SV's methods, this distance d should be the bonding length between exact atomic positions with positively charge cores, representing the real force center of each atom. Based on our assumption, the d distance is defined as the spatial separation between two nearest neighbor superatom positions, $d=3.257$ Å. Although it remains disputable whether the center of mass of the C4 superatom could be assigned its real force center (thus allowing the applicability of Gao's and SV's models) the high strength and rigidity of each individual C4 unit manifested by the dense and strong carbon-carbon bonds seem to validate this assumption of d distance. Obviously, each superatom contains 16 valence electrons, and $N_e = 8/26.61 = 0.3$. By inserting these values of d and N_e in Gao's formula (Eq. 1), we derive a Vickers hardness of 8.2 GPa, in agreement with our value of 5.6 GPa. To apply the same adjustment to the SV model one needs to define the crucial parameter R_i for the superatom. From our first-principles calculations, it can be inferred that $R_i = 2.32$ Å represents the optimum radius containing all 16 valence electrons for each superatom. By inserting $e_i = 16/2.32 = 6.896$ in Eq. 2 a Vickers hardness of 7.7 GPa is obtained, again in agreement with our analysis. Within this superatom approach, all three methods discussed in the present paper convey the same answer: T-carbon is not superhard. The anomalous behavior of Gao and SV models observed in Fig.2 for T-carbon is cured and the general agreement among the three Gao, SV and Chen models is re-established. This provides clear evidence that the hardness of T-carbon should not exceed 10 GPa.

Acknowledgements We greatly appreciate the thought of the treatment of "superatom" to successfully apply Gao et al.'s model to hardness of T-carbon from Prof. Faming Gao and useful discussions with Prof. Gang Su and Dr. D.-E. Jiang for his critical reading. X. -Q. C. acknowledges the support from the "Hundred Talents Project" of CAS and the NSFC (Grant No. 51074151). The authors also acknowledge the computational resources from the Supercomputing Center (including its Shenyang Branch in the IMR) of CAS.

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